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(54) STEEL FOR USE AT HIGH TEMPERATURES

(71) We, DALMINE S.P.A., an Italian Company, of 19, Via Brera, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to steel for use at high temperatures. More specifically, the invention relates to a low-alloy ferritic steel with high creep resistance for operating temperatures of up to 575°C., and reasonable ductility and toughness properties at room temperature. The invention is also concerned with those treatments to which the steel must be subjected to acquire the desired properties.

The problems involved in the use of steel for the manufacture of high temperature operating equipment such as chemical reactors, boilers, boiler pipes and steam ducts are very important and are connected to the cold-workability of the steel and to its life at the service temperature. In fact, ordinary steels having good cold-workability qualities present particularly important problems in relation to creep such that the life of an article made of such steels is considerably shortened. On the other hand, for those steels with good creep resistance qualities, certain problems regarding cold-workability are encountered. However, since steel is the only relatively low cost material which can be used at temperatures of up to 800 or 1000°C., many classes of steels for use at such temperatures have been developed.

It can be said that high-temperature steels can be grouped into three main classes:—

1. high-nickel and chromium-containing austenitic steels, usable at temperatures of the order of 900 to 1000°C.;
2. ferritic steels with no nickel and containing up to 12% by weight chromium for use at temperatures up to about 800°C.;
3. low-alloy ferritic steels, almost all of them nickel-free, and containing up to about 5% by weight chromium, for use at temperatures up to about 600°C.

The steel of this invention belongs to this latter class, which includes several low-alloy steels for use at temperatures up to about 600°C. For example, Japanese Patent Specification No. 72.47488 relates to a steel with the following weight percentage composition: 0.15 to 0.32 C; 0.05 to 0.35 Si; 0.2 to 0.8 Mn; 0.5 to 3.0 Cr; 0.3 to 1.5 Mo; 0.1 to 0.35 V; either Ta or Nb 0.05 to 0.5; and 0.02 to 0.1 N; the balance being iron. The advantage of this steel is that its creep strength is about twice that recorded for conventional Cr-Mo-V steels.

Soviet Patent Specification No. 338551 relates to a steel with the following weight percentage composition: 0.38 to 0.44 C; 0.3 to 0.6 Mn; 0.17 to 0.37 Si; 2 to 5 Cr; 1.2 to 1.6 Ni; 1.4 to 1.8 Mo; 0.25 to 0.4 V; 0.03 S; and 0.03 P; the balance being iron. With such a composition the steel has a considerable toughness and it is usable for hot-pressing of Al alloy sections.

Japanese Patent Specification No. 73.13803 relates to a steel with a high creep strength at temperatures below 500°C., which is weldable and has good toughness properties. Its weight percentage composition is: 0.08 to 0.20 C; 0.20 to 0.40 Si; 1.0 to 1.6 Mn; 0.05 to 0.35 Cr; 0.10 to 0.60 Mo; 0.005 to 0.10 V; 0.0004 to 0.02 N; the balance being iron. B (0.001 to 0.01%) and Nb (0.01 to 0.05%) can also be added.

British Patent Specification No. 1,218,927

relates to a steel having the following weight percentage composition: 0.21 to 0.35 C; <0.35 Si; 0.39 to 1 Mn; 0.4 to 1 Ni; 0.7 to 1.4 Cr; 0.5 to 1.5 Mo; 0.2 to 0.6 V; 0.03 to 0.15 Ti + Nb and/or Ta; 0.002 to 0.01 B; 0.5 to 3 Co; the balance being iron. This steel is particularly recommended for turbine shafts for aircraft engines or parts of steam and gas turbines.

Japanese Patent Specification No. 71.27656 relates to a steel having the following weight percentage composition: <0.3 C; 0.1 to 0.5 Si; 0.2 to 1.5 Mn; <0.01 Al; 0.004 to 0.02 N; 0.002 to 0.1 Se and/or Te, and, if required, 0.2 to 1.0 Cr and 0.1 to 1.2 Mo; the balance being iron. This steel is particularly suited for high-temperature and pressure boilers.

Finally, United States Patent Specification No. 3,607,238 concerns a steel with the following weight percentage composition: 0.20 to 0.30 C; 0.4 to 1.0 Mn; 0.4 to 1.0 Ni; preferably Mn + Ni equalling 1.5%; 0.7 to 1.4 Cr; 0.5 to 1.5 Mo; 0.25 to 0.40 V; 0.003 to 0.5 Nb and 0.002 to 0.010 B; the balance being iron.

The steel of the present invention is a low-chromium steel and it is particularly recommended for seamless tubes used at a maximum operating temperature of 575°C; however, its good weldability qualities make it suitable also for the production of welded parts as, for example, boiler parts, large steam ducts and so on.

The invention provides a steel in which the low content of the alloying elements makes manufacturing easier and more economical, with no prejudice to the properties of creep strength, impact and workability; the ultimate creep elongation shows a steady value for rupture times of up to 10,000 hours.

The steel composition, together with appropriate thermal treatment of the steel, makes it possible to attain an optimal balance between the workability and weldability qualities of the steel and the hot-strength properties of the steel. Consequently, the use of this steel is particularly convenient for cost reasons and its easy application and fairly good heat-resistance.

The composition of the steel has been so selected as to make its manufacture relatively economical as well as to give it high properties of creep resistance, ductility and toughness at room temperature.

According to the invention, the weight percentage composition of the steel is as follows: 0.04 to 0.08 C; 0.9 to 1.2 Cr; 0.9 to 1.1 Mo; 0.20 to 0.25 V; 0.14 to 0.18 Nb; 0 to 0.006 B; <0.50 Si; <1.0 Mn; N between 100 and 130 p.p.m.; the balance being iron and incidental impurities. The percentages of the different elements have been studied in order to obtain the best final results; particularly, there are specific relationships between certain elements which form this steel. In practice, it has been found that an accurate stoichiometric ratio between carbon, nitrogen, vanadium and niobium is required to obtain the above-mentioned qualities. Consequently, the steel which is the subject of this invention is characterised by its general composition as well as in that the sum of the percentages of vanadium and niobium is preferably between 0.35 to 0.40%, and that the sum of the percentages of niobium and vanadium is related to the sum of the percentages of carbon and nitrogen according to the formula:

$$(C + N) < \left(\frac{V}{4} + \frac{Nb}{8}\right) < 1.2\ (C + N)$$

The purpose of this invention is to supply a low-alloy ferritic-bainitic steel whose properties are obtained after precipitation hardening. Therefore, the carbon content is kept as low as possible, compatible with the usual oxygen blowing techniques, in order to obtain a steel with good weldability qualities. Both niobium and vanadium are added to an extent just sufficient to combine with the carbon and nitrogen present in the melt by forming carbides and carbonitrides. These cause hardening of the ferritic matrix when they are precipitated in adequate amounts and distributed by the appropriate thermal treatment which will be discussed later. Also molybdenum is added so that it induces hardening by solid solution. Chromium is added to favour hot-oxidation resistance; however, its content should not exceed 1% so as to avoid its negative influence on creep resistance. Boron may be added to increase hot ductility and hardenability of the steel.

It has been found that the most appropriate precipitation heat treatment for the steel of this invention is normalisation from 1000 to 1200°C. followed by tempering at between 600 and 800°C. The qualities which can be obtained from steel, normalised from 1050°C. and tempered at between 700 and 720°C., will be set out below by way of example with reference to those of another steel currently used at maximum temperatures of 575°C. This reference steel, already available in the trade, has the following percentage composition by weight: 0.11 C; 0.40 Cr; 0.60 Mo; 0.25 V; the balance being iron together with the usual percentage contents of Si, Mn, S and P.

Table 1 shows a comparison between the impact strengths of the steels; the steel according to the present invention was normalised from 1050°C., while the reference steel was normalised from 960°C., this being the temperature recommended for the industrial production of the reference steel, and which imparts to that steel the best properties. The impact strength characteristics are given as a function of the tempering temperature.

TABLE 1

Tempering temperature		700°C.	750°C.	800°C.
Steel		Charpy – V – kgm.		
Steel obtained according to the invention	Casting A	23.9 – 24.2	24.1 – 25.0	22.0 – 24.4
	Casting B	24.0 – 24.2	24.3 – 25.2	21.8 – 24.0
	Casting C	23.6 – 24.3	24.5 – 26.0	21.9 – 23.8
	Casting D	23.9 – 24.1	24.3 – 24.9	21.2 – 23.3
	Casting E	24.1 – 24.3	24.2 – 24.8	21.5 – 24.0
	Casting F	23.8 – 24.2	24.0 – 24.5	22.0 – 23.7
	Reference steel 1	5.3 – 8.4	8.4 – 10.6	5.0 – 5.5
	Reference steel 2	4.2 – 8.0	7.3 – 9.9	4.4 – 5.3

It is evident from this table that the steel which is the subject of this invention has, as compared to the reference steel, considerably higher average impact strength properties as well as more consistent impact strength properties in the field of tempering temperatures explored, so that the exact achievement of the tempering temperature may be non-critical.

Therefore, the steel of the invention shows far higher toughness qualities than those found in the steel now used in the trade. It has also shown good weldability qualities; far better than those shown by the reference steel.

Tables 2 and 3 respectively show the comparisons between the steels specified in Table 1, as compared to breaking stresses in 10^5 hours (Table 2) and to % elongations after breaking due to creep. The steels were normalised from 1050°C. and tempered at between 700 and 720°C.

TABLE 2

	Breaking stress in 10^5 hours kg/mm^2		
Test temperature	500°C.	550°C.	600°C.
Steel			
Casting A	24 – 26	15.5 – 18	10 – 11
Casting B	25 – 26.5	15 – 16.5	9.5 – 11
Casting C	24.5 – 25.5	16 – 17	10.5 – 12
Casting D	23.5 – 24.5	16 – 16.5	11
Casting E	15 – 26	16 – 17	11 – 12.5
Casting F	25 – 26.5	15 – 18	10 – 11.5
Reference 1	14.8 – 18.5	8.5 – 10	3.1 – 3.8
Reference 2	15.3 – 19.8	8.2 – 9.3	3.1 – 4.2

TABLE 3

	Elongation after breaking due to creep at 550°C.		
breaking time hours	100	1000	10.000
Steel			
Casting A	19 – 22	18 – 20	17 – 19
Casting B	20 – 21	18 – 19	15 – 16
Casting C	21 – 22	19 – 20	16 – 18
Casting D	18 – 20	19 – 26	17 – 19
Casting E	20 – 21	17 – 19	15 – 16
Casting F	20 – 21	18 – 19	14 – 16
Reference 1	18 – 20	17 – 20	15 – 18
Reference 2	18 – 21	18 – 20	16 – 18

As shown in Table 2, the steel of this invention has higher breaking stresses than those found in the reference steel and it also has a similar improved ductility (Table 3). In conclusion, the steel of this invention represents a considerable development as compared to the reference steel as a result of its cold-workability and hot-strength qualities. It also represents a considerable advance with regard to other steels because of its economical manufacture and its general qualities.

WHAT WE CLAIM IS:—

1. A low-alloy ferritic steel for use at operating temperatures up to 575°C., said steel having the following weight percentage composition: 0.04 to 0.08 C; 0.9 to 1.2 Cr; 0.9 to 1.1 Mo; 0.20 to 0.25 V; 0.14 to 0.18 Nb; 0 to 0.006 B; <0.50 Si; <1.0 Mn; 100 to 130 p.p.m. nitrogen; the balance being iron and incidental impurities.

2. Steel according to claim 1, in which the sum of the weight percentages of V and Nb is between 0.35 and 0.40 and in which this sum is related to the sum of the C and N percentages by the formula:

$$(C + N) < \left(\frac{V}{4} + \frac{Nb}{8}\right) < 1.2\,(C + N)$$

3. A process which involves providing a steel having a composition according to claim 1 or claim 2, normalising the steel from 1000 to 1200°C. and tempering it at between 600 and 800°C.

4. A low-alloy ferritic-bainitic steel having a composition according to claim 1 and substantially as hereinbefore described.

5. A method of manufacturing steel articles which includes the use of a steel having a composition according to claim 1, said steel being normalised and tempered.

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